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Changes in the Setting Time of Portland Cement.

THE earlier work of P. Schachtschabel on the setting of Portland cement has already been described in this journal (February, 1932). It has now been continued by a comprehensive series of experiments on the changes in setting time due to exposure to air, dealing both with the change from normal to quick setting and the reverse. Cements of high alkali content containing 3 per cent. gypsum were used, since high-alkali cements are most susceptible to change.

According to *Zement*, it was found that both CO_2 and water vapour must be present in the air to render a cement quick-setting on storage. The amount of water vapour is the predominating factor. The change from normal to quick set only occurs in air of fairly low moisture content. In saturated air a quick-setting cement will become slow setting. Rotary-kiln cements are not nearly so susceptible to changes in setting time as shaft-kiln cements.

The suggested mechanism of these changes is as follows. In air of moderate moisture content the alkaline compounds in cement first absorb moisture to form hydrates. These are then decomposed by the CO_2 to form alkali carbonates, which by destroying part of the gypsum present render the cement quick setting. In air saturated with moisture hydrate formation extends to the tricalcium aluminate. The anhydrous aluminate is a powerful accelerator, but the hexahydrate formed in moist air is not. The cement therefore becomes slow setting. In the presence of this second reaction the formation of alkali carbonates has no effect, or may even have a retarding action, depending on the setting time of the ungypsumised cement. In addition to the chemical aspect this retardation of set is also aided by physical causes, since each cement particle becomes surrounded by a layer of hydrated material which has a retarding effect. Experiments with normal and overburnt clinker showed that the retarding action of saturated air is much more pronounced with the overburnt clinker. The amount of CaO

and $Ca(OH)_2$ in the cement has very little effect in causing changes of setting time.

The following practical suggestions for the avoidance of changes in setting time emerge from the work. Since the primary cause is the alkali content of the cement the alkali content of the raw mix should not be too high. The raw materials should be well mixed and the clinker well burnt. When possible the ground clinker, without gypsum, should have initial set of not less than five minutes. Grinding must receive careful attention. The conversion of gypsum to hemihydrate is a frequent cause of change in setting time, although some dehydration in the mill is advantageous. The use of mills fitted with screens improves the results. The addition of 0.5 to 1.0 per cent. $CaCl_2$ or $MgCl_2$ in the mill is valuable where the exit temperature is below 90 to 100 deg. C. With exit temperatures above 110 deg. C. the gypsum should not exceed 2.0 to 2.5 per cent. or false set will occur. If it is essential to exceed 2.5 per cent. gypsum false set can be prevented by adding 0.25 to 0.5 per cent. crude NaCl to the clinker, or by mixing ground gypsum with the cement after it leaves the mill. Natural anhydrite should not be used with cements susceptible to changes in setting time.

Change of setting time in the silo is not probable ; the change occurs later when the cement is filled into paper sacks. Raw materials containing more than 0.7 per cent. alkalis (oxides) can only be burnt in the shaft kiln if the greatest care is exercised. Raw materials containing up to 1.2 per cent. alkalis can be burnt in the rotary kiln. High alkali content has the added disadvantage that the kiln lining is rapidly attacked.

The Portland Cement Industry in Spain.

The position of the Spanish cement industry last year was affected by the diminution of sales in the home market and also by the starting of new plants. At the end of 1931 the total capacity of the twenty-three principal Portland cement mills in Spain was 2,260,000 metric tons per year, while at the end of 1932 it was 2,308,000 metric tons, an increase of about 2½ per cent. To this may be added a new mill at Morata de Jalón (Zaragoza) opened early this year with a capacity of 60,000 tons.

The sales of the twenty-three concerns were 1,308,000 metric tons in 1932, against 1,431,000 tons in 1931, or a decrease of 8½ per cent. Thus the percentage of production to capacity has decreased from 63.3 in 1931 to 56.7 per cent. in 1932.

Exports reached the figure of 31,000 tons in 1932, including cement shipped to foreign countries and to the Spanish Protectorate in Morocco, Spanish Guinea, and the Canary Islands. It is felt that the prospects for 1933 have improved a little, because unemployment is to be relieved by the inauguration of many important public works.

Heat Transmission in Rotary Kilns—II.

By WM. GILBERT, Wh.Sc., M.Inst.C.E.

(22) In this article various formulæ and tables are provided for use later in connection with heat transmission calculations. They relate chiefly to radiation from hot solid bodies and from gases, and also to convection. A certain amount of explanation is given in order that the data may be rightly used.

Black Body Radiation.

The quantity of heat which can be radiated from a hot body (such as a firebrick) depends partly on the nature of the surface and partly on the temperature, but for each temperature the heat radiated has a definite limiting value which cannot be exceeded whatever the nature of the surface may be. It is convenient in practice to tabulate these limiting values (expressed in B.T.U.'s per square foot per minute) against a suitable range of temperatures. Figures taken from the table are reduced when required in accordance with the nature of the surface and the other conditions of each problem.

The formula for maximum radiation (termed black body radiation) has been well established by experiment. It is as follows:

$$Q = \frac{1.73 \times T^4}{60 \times 10^9} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where Q = heat radiated in B.T.U.'s per square foot per minute.

T = absolute temperature of the radiating surface in degrees F.

The absolute temperature of a body is found by adding 461 to the temperature in degrees F.

(23) Table No. 1 has been calculated from the formula; the value of the black body radiation is placed opposite the ordinary (not the absolute) temperature in each case. The figures in the difference columns enable the radiation to be readily obtained for each degree between 0 and 2,590 deg. F.

Heat is radiated by a group of very short waves; the maximum intensity of radiation at the higher temperatures usual in rotary kilns occurs at a wave length of approximately $\frac{1}{12{,}000}$ in.

(24) To illustrate the use of Table I let *Fig.* 3 represent two parallel plates *A* and *B* each 1 ft. square, the plates being placed sufficiently close together so that the loss of radiation endways can be neglected. The inner surface of each plate is assumed to emit black body radiation. Further, let plate *A* be maintained at a temperature of 1,800 deg. F and plate *B* at 600 deg. F. The rate of heat supply from plate *A* to plate *B* in B.T.U.'s per square foot per minute can be obtained from Table I as shown below.

1,800 deg. F.	=	753.5
600 deg. F.	=	36.5
Difference, or rate of heat supply	=	717.0

TABLE I.

BLACK BODY RADIATION IN B.T.U. PER SQUARE FOOT PER MINUTE.

Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.	Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.	Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.
0	1.3	0.01	290	9.2	0.05	580	33.9	0.13
10	1.4	0.01	300	9.7	0.05	590	35.2	0.13
20	1.5	0.01	310	10.2	0.05	600	36.5	0.13
30	1.6	0.01	320	10.7	0.05	610	37.9	0.14
40	1.7	0.02	330	11.3	0.06	620	39.3	0.14
50	1.9	0.02	340	11.9	0.06	630	40.8	0.15
60	2.1	0.02	350	12.5	0.06	640	42.3	0.15
70	2.3	0.02	360	13.1	0.06	650	43.9	0.16
80	2.5	0.02	370	13.7	0.06	660	45.5	0.16
90	2.7	0.02	380	14.4	0.07	670	47.2	0.17
100	2.9	0.02	390	15.1	0.07	680	48.9	0.17
110	3.1	0.02	400	15.8	0.07	690	50.6	0.17
120	3.3	0.02	410	16.6	0.08	700	52.4	0.18
130	3.5	0.02	420	17.4	0.08	710	54.2	0.18
140	3.7	0.03	430	18.2	0.08	720	56.1	0.19
150	4.0	0.03	440	19.0	0.08	730	58.0	0.19
160	4.3	0.03	450	19.9	0.09	740	60.0	0.20
170	4.6	0.03	460	20.8	0.09	750	62.0	0.20
180	4.9	0.03	470	21.7	0.09	760	64.1	0.21
190	5.2	0.03	480	22.6	0.09	770	66.2	0.21
200	5.5	0.03	490	23.6	0.10	780	68.3	0.21
210	5.8	0.03	500	24.6	0.10	790	70.6	0.23
220	6.2	0.04	510	25.6	0.10	800	72.9	0.23
230	6.6	0.04	520	26.7	0.11	810	75.2	0.23
240	7.0	0.04	530	27.8	0.11	820	77.6	0.24
250	7.4	0.04	540	28.9	0.11	830	80.0	0.24
260	7.8	0.04	550	30.1	0.12	840	82.5	0.25
270	8.2	0.04	560	31.3	0.12	850	85.1	0.26
280	8.7	0.05	570	32.6	0.13	860	87.8	0.27

TABLE I.—(*Continued.*)

BLACK BODY RADIATION IN B.T.U. PER SQUARE FOOT PER MINUTE.

Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.	Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.	Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.
870	90.5	0.27	1,160	199.1	0.49	1,450	384.6	0.80
880	93.2	0.27	1,170	204.0	0.49	1,460	392.7	0.81
890	96.0	0.28	1,180	209.0	0.50	1,470	400.9	0.82
900	98.9	0.29	1,190	214.3	0.53	1,480	409.3	0.84
910	101.8	0.29	1,200	219.6	0.53	1,490	417.8	0.85
920	104.8	0.30	1,210	224.9	0.53	1,500	426.4	0.86
930	107.9	0.31	1,220	230.3	0.54	1,510	435.2	0.88
940	111.0	0.31	1,230	235.8	0.55	1,520	444.1	0.89
950	114.2	0.32	1,240	241.3	0.55	1,530	453.1	0.90
960	117.5	0.33	1,250	247.0	0.57	1,540	462.3	0.92
970	120.9	0.34	1,260	252.7	0.57	1,550	471.6	0.93
980	124.3	0.34	1,270	258.6	0.59	1,560	481.0	0.94
990	127.8	0.35	1,280	264.6	0.60	1,570	490.6	0.96
1,000	131.4	0.36	1,290	270.8	0.62	1,580	500.3	0.97
1,010	135.0	0.36	1,300	277.1	0.63	1,590	510.2	0.99
1,020	138.7	0.37	1,310	283.4	0.63	1,600	520.3	1.01
1,030	142.5	0.38	1,320	289.9	0.65	1,610	530.4	1.01
1,040	146.4	0.39	1,330	296.6	0.67	1,620	540.7	1.03
1,050	150.3	0.39	1,340	303.3	0.67	1,630	551.2	1.05
1,060	154.3	0.40	1,350	310.1	0.68	1,640	561.8	1.06
1,070	158.4	0.41	1,360	317.0	0.69	1,650	572.6	1.08
1,080	162.6	0.42	1,370	324.0	0.70	1,660	583.5	1.09
1,090	166.8	0.42	1,380	331.2	0.72	1,670	594.6	1.11
1,100	171.2	0.44	1,390	338.4	0.72	1,680	605.9	1.13
1,110	175.7	0.45	1,400	345.7	0.73	1,690	617.3	1.14
1,120	180.2	0.45	1,410	353.2	0.75	1,700	628.8	1.15
1,130	184.8	0.46	1,420	360.9	0.77	1,710	640.5	1.17
1,140	189.4	0.46	1,430	368.7	0.78	1,720	652.4	1.19
1,150	194.2	0.48	1,440	376.6	0.79	1,730	664.4	1.20

TABLE I.—(*Continued.*)

BLACK BODY RADIATION IN B.T.U. PER SQUARE FOOT PER MINUTE.

Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.	Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.	Temperature Fahr.	$\frac{1.73 \times T^4}{60 \times 10^9}$	Diff. per deg. Fahr.
1,740	676.7	1.23	2,030	1,110	1.8	2,320	1,725	2.5
1,750	689.1	1.24	2,040	1,128	1.8	2,330	1,750	2.5
1,760	701.6	1.25	2,050	1,146	1.8	2,340	1,775	2.5
1,770	714.3	1.27	2,060	1,164	1.8	2,350	1,800	2.5
1,780	727.2	1.29	2,070	1,183	1.9	2,360	1,826	2.6
1,790	740.3	1.31	2,080	1,202	1.9	2,370	1,852	2.6
1,800	753.5	1.32	2,090	1,221	1.9	2,380	1,878	2.6
1,810	766.9	1.34	2,100	1,240	1.9	2,390	1,905	2.7
1,820	780.5	1.36	2,110	1,260	2.0	2,400	1,932	2.7
1,830	794.3	1.38	2,120	1,280	2.0	2,410	1,959	2.7
1,840	808.3	1.40	2,130	1,300	2.0	2,420	1,986	2.7
1,850	822.4	1.41	2,140	1,320	2.0	2,430	2,014	2.8
1,860	836.8	1.44	2,150	1,340	2.0	2,440	2,042	2.8
1,870	851.3	1.45	2,160	1,361	2.1	2,450	2,070	2.8
1,880	866.0	1.47	2,170	1,382	2.1	2,460	2,099	2.9
1,890	880.8	1.48	2,180	1,403	2.1	2,470	2,128	2.9
1,900	896.0	1.52	2,190	1,424	2.1	2,480	2,157	2.9
1,910	911.2	1.52	2,200	1,446	2.2	2,490	2,186	2.9
1,920	926.7	1.55	2,210	1,468	2.2	2,500	2,216	3.0
1,930	942.3	1.56	2,220	1,490	2.2	2,510	2,246	3.0
1,940	958.2	1.59	2,230	1,512	2.2	2,520	2,277	3.1
1,950	974.3	1.61	2,240	1,534	2.2	2,530	2,308	3.1
1,960	990.5	1.62	2,250	1,557	2.3	2,540	2,339	3.1
1,970	1,007	1.65	2,260	1,580	2.3	2,550	2,370	3.1
1,980	1,024	1.7	2,270	1,604	2.4	2,560	2,402	3.2
1,990	1,041	1.7	2,280	1,628	2.4	2,570	2,434	3.2
2,000	1,058	1.7	2,290	1,652	2.4	2,580	2,466	3.2
2,010	1,075	1.7	2,300	1,676	2.4	2,590	2,498	3.2
2,020	1,092	1.7	2,310	1,700	2.4			

It is important to notice that not only can plate *A* send to plate *B* the black body radiation due to a temperature of 1,800 deg. F., but plate *B* can send to plate *A* the black body radiation due to a temperature of 600 deg. F., so that the difference has to be taken. This conception appears to have first occurred to Prévost, of Geneva, in 1792, and it is known as Prévost's Theory of Exchanges.

A second example, where neither plate is a full radiator, is worked out in Appendix I, the object being to illustrate the following general principles: (*a*) The absorbing and the radiating powers of any given surface are equal; (*b*) A surface will reflect, or scatter back, the proportion of radiated or reflected heat falling on it which it is unable to absorb.

Radiation from the Gases H_2O and CO_2.

(25) Tyndall found by experiment that the gases H_2O and CO_2 could absorb (and consequently radiate) considerable quantities of heat, but it is only during the past few years that attempts have been made to develop and use this knowledge in engineering practice. A rotary kiln in operation is filled with mixed gases from end to end, and the quantity of heat which can be radiated to the material, or to the kiln lining, at any cross section depends upon (*a*) the tempera-

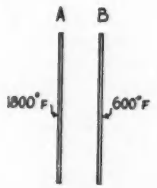


Fig. 3.

ture of the gas; (*b*) the diameter of the gas column (which is the same as the internal diameter of the kiln); (*c*) the fraction of CO_2 or H_2O present in the mixed gas, the estimation being made by volume.

The radiation from the CO_2 and from the H_2O has to be estimated separately. Where the two gases occur together (as they do in a rotary kiln) a certain reduction is made since each gas interferes to some extent with the radiation from the other.

(26) The subject of gas radiation has been recently investigated by Professor H. C. Hottel, of the Massachusetts Institute of Technology (see *Industrial and Engineering Chemistry*, August, 1927), and more recently Professor Hottel supplied the writer with some revised data from which the figures given in Tables II, III and IV have been prepared. The position appears to be that the quantity of heat which can be radiated from a volume of CO_2 under various conditions is fairly well established, but further experiments now in progress may somewhat modify the figures given for the radiation from water vapour.

TABLE II.

RADIATION DUE TO WATER VAPOUR.

B.T.U. per square foot per minute.

Temperature Fahr.	Values of P.D.										
	0.25	0.30	0.40	0.50	0.60	0.80	1.0	1.5	2.0	3.0	4.0
300	1.3	1.5	1.8	2.1	2.3	2.6	2.9	3.3	3.6	3.9	4.1
400	2.0	2.3	2.9	3.3	3.6	4.2	4.7	5.5	5.9	6.4	6.9
500	3.0	3.5	4.3	4.9	5.4	6.4	7.1	8.3	9.0	10.0	10.7
600	4.3	4.9	6.1	6.9	7.7	9.1	10.2	12.0	13.2	14.7	16.0
700	5.9	6.7	8.3	9.5	10.6	11.2	14.4	17.0	18.9	21.1	22.5
800	7.8	8.9	11.1	12.8	14.4	17.4	19.7	23.1	25.4	28.5	30.8
900	10.3	11.7	14.7	16.7	19.3	22.9	25.7	30.5	34.3	37.9	41.2
1,000	13.0	15.0	18.9	21.8	24.3	29.3	32.8	39.5	44.0	49.3	53.6
1,100	16.0	18.9	23.3	26.8	30.3	37.1	40.8	50.0	55.7	62.7	68.5
1,200	20.3	23.3	28.7	33.5	38.0	46.2	51.7	62.8	70.4	79.2	87.1
1,300	24.3	28.3	34.9	40.8	46.2	55.9	63.5	77.4	87.5	99.2	108.0
1,400	29.1	33.8	41.7	49.6	55.5	68.0	76.6	95.3	107.2	121.7	130.3
1,500	34.5	39.9	50.0	58.3	66.7	81.3	91.7	113.8	128.2	147.1	160.0
1,600	40.3	47.1	58.3	69.8	78.4	96.4	109.5	135.1	152.8	177.1	192.5
1,700	47.3	54.9	68.5	81.4	92.8	112.7	128.3	161.9	183.8	210.8	228.3
1,800	54.5	63.5	79.4	94.9	107.6	130.6	150.0	189.6	215.8	246.5	268.9
1,900	62.3	73.0	91.7	109.0	123.3	151.5	175.9	217.8	249.7	286.3	313.1
2,000	70.8	83.3	104.0	124.0	140.3	175.5	200.0	248.2	285.5	328.8	362.5
2,100	80.5	94.6	118.0	141.3	159.5	200.0	226.7	284.0	328.6	379.1	413.7
2,200	91.7	107.2	133.3	160.8	183.6	223.9	257.7	325.2	378.7	433.3	477.8
2,300	102.8	119.5	148.8	181.8	205.6	252.5	288.8	368.8	425.6	491.7	543.0
2,400	113.7	133.3	168.7	202.3	227.7	280.8	325.0	408.3	480.8	554.1	611.1
2,500	126.2	146.8	187.2	222.2	253.2	311.7	363.5	458.3	536.6	620.5	686.5

TABLE III.

RADIATION DUE TO CO_2.

B.T.U. per square foot per minute.

Temperature Fahr.	Values of P.D.				Temperature Fahr.	Values of P.D.			
	0.5	1.0	2.0	4.0		0.5	1.0	2.0	4.0
300	0.88	1.08	1.17	1.29	1,500	37.2	41.7	44.9	47.7
400	1.50	1.78	1.89	2.05	1,600	44.1	50.0	53.5	57.4
500	2.40	2.71	2.91	3.07	1,700	51.8	59.2	63.4	68.6
600	3.50	3.95	4.19	4.38	1,800	60.0	69.3	73.5	80.0
700	5.0	5.6	5.92	6.19	1,900	69.4	79.6	86.0	93.0
800	7.2	7.6	8.12	8.37	2,000	78.7	91.7	98.2	105.6
900	9.3	10.3	11.0	11.4	2,100	89.9	103.0	111.4	120.0
1,000	12.2	13.5	14.4	14.9	2,200	100.0	116.0	125.3	133.3
1,100	15.7	17.5	18.7	19.5	2,300	111.8	127.9	139.9	151.8
1,200	20.5	22.4	24.0	25.0	2,400	122.8	141.7	155.2	170.8
1,300	25.3	28.2	30.0	31.3	2,500	133.2	157.4	173.3	190.2
1,400	30.9	34.6	37.0	39.0					

Radiation Due to Water Vapour.

(27) The radiation due to water vapour (H_2O) is given in Table II. At each gas temperature the radiation in B.T.U.'s per square foot per minute is given for a series of values of the product *PD* where

P = The partial pressure of the vapour, or in other words the fraction present by volume.

D = Diameter of gas column in feet.

The figures given in the Table are the radiation from the circumference of the gas column to the inner surface of the lining, per square foot of lining area.

(28) The radiation due to CO_2 is given in a similar manner in Table III, and the correction for shielding when the two gases occur together is given in Table IV.

To obtain intermediate values graphs plotted on squared paper with millimetre ruling, from the figures given in the three tables, will be found very useful. For instance, *Fig.* 4 shows a graph for the radiation due to water vapour between the temperatures of 1,000 deg. and 2,500 deg. F. It is convenient to plot the portion from 300 deg. to 1,000 deg. F. to ten times the vertical scale used in *Fig.* 4.

(29) As an example of the use of Tables II, III and IV we may take a cross section of a rotary kiln where the internal diameter is 8 ft. and the gas temperature 1,500 deg. F. The proportion of H_2O by volume is 0.248, and the proportion of CO_2 is 0.157, hence we have

Value of *PD* for $H_2O = 0.248 \times 8 = 1.98$.

From Table II, at 1,500 deg. F. the corresponding radiation is 128.

Similarly for the CO_2 the value of *PD* is $0.157 \times 8 = 1.26$, and from Table III at 1,500 deg. F., by interpolation, the radiation is 42.5. To estimate the reduction due to shielding, the two values of *PD* have to be added. Their sum

TABLE IV.

CORRECTION FOR SHIELDING.

B.T.U. per square foot per minute.

Temperature Fahr.	Values of P.D. (added)					
	1.0	1.5	2.0	3.0	4.0	6.0
600	—	—	—	—	0.19	0.23
700	—	0.22	0.28	0.34	0.41	0.47
800	0.28	0.41	0.52	0.65	0.76	0.90
900	0.50	0.71	0.90	1.13	1.33	1.56
1,000	0.79	1.13	1.44	1.82	2.16	2.50
1,100	1.20	1.73	2.23	2.77	3.24	3.81
1,200	1.74	2.50	3.18	3.96	4.65	5.45
1,300	2.43	3.47	4.43	5.58	6.53	7.67
1,400	3.24	4.66	5.93	7.50	8.80	10.21
1,600	5.34	7.72	9.78	12.33	14.37	16.67
1,800	7.92	11.4	14.45	18.45	21.61	25.00
2,000	11.00	16.0	20.53	25.63	29.90	34.70
2,200	14.71	21.7	27.25	33.88	39.83	46.30
2,400	19.50	27.8	35.07	43.37	51.38	59.82
2,600	24.07	34.5	43.75	54.90	64.28	75.00

is 1.98 + 1.26 = 3.24, and from Table IV, at 1,500 deg. F., the reduction required is 10.2. Hence the actual value of the mixed gas radiation, per square foot of lining surface per minute, is 128 + 42.5 − 10.2 = 160.3 B.T.U.'s.

If the emission (or the absorption) coefficient of the firebrick is taken to be 0.9, the heat actually absorbed by the lining is 0.9 × 160.3 = 144.3 B.T.U.'s per square foot per minute. The balance of 16 B.T.U.'s is reflected back to the gas.

(30) If the gas column were treated as a solid at a temperature of 1,500 deg. F., the maximum quantity of heat which it could radiate as a black body, from Table I, is 426.4 B.T.U.'s per square foot per minute, hence the gas radiation is 37.6 per cent. of black body radiation. This rather high value is due to the large percentage of water vapour present in the wet end of a rotary kiln. Methods of estimating the gas radiation when the gas shape is not cylindrical are given in Professor Hottel's paper [see para. (26)].

Radiation from Incandescent Coal Particles.

(31) As stated in Part I, para. (8), approximately 50 per cent. of the heat transmission in an average kiln is due to radiation from the incandescent coal particles; hence it is necessary to give careful attention to this subject. For calculation purposes all the coal particles are assumed to be spheres of the same size, and the error produced by doing so, on the length calculated for the kiln, is probably small. The diameter of a coal particle is here always expressed in units of $\frac{1}{10,000}$ inch.

Referring again to the kiln 202 ft. in length [see Part I, para. (3)], the average diameter of the coal particles, as ground, was seven units, which means that a pound of such particles would have the same surface area that a pound of the ground coal actually had.

In the kiln combustion takes place over a length of about 35 ft., the volume inside the lining being filled with incandescent coal or coke particles more or less consumed. Their pitch, or distance apart if uniformly distributed, is approximately 238 units, or $\frac{1}{42}$ inch. This is thirty-four times the average particle diameter as ground. Near the beginning of the combustion zone the volatile matter is driven off in about one-tenth of the time required for complete combustion. The resulting coke particle burns to CO_2, and it is assumed to radiate heat from its surface at a temperature of 2,450 deg. F. until it is entirely consumed, no account being taken of the remaining ash.

(32) A longitudinal section of the combustion zone is shown in *Fig.* 5. It is required to determine the quantity of radiation, expressed in B.T.U.'s per square foot per minute, which falls upon a small area of the firebrick lining such as that marked B on the cross section AA near the centre of the cone. Each coal particle such as G, H or K radiates heat in all directions, and a proportion of it reaches B, although the effect of particles beyond the sections EE and FF, distant one kiln diameter from *AA*, is small. A considerable proportion of the radiation from *G*, *H* or *K* will be intercepted by other particles, but Professor

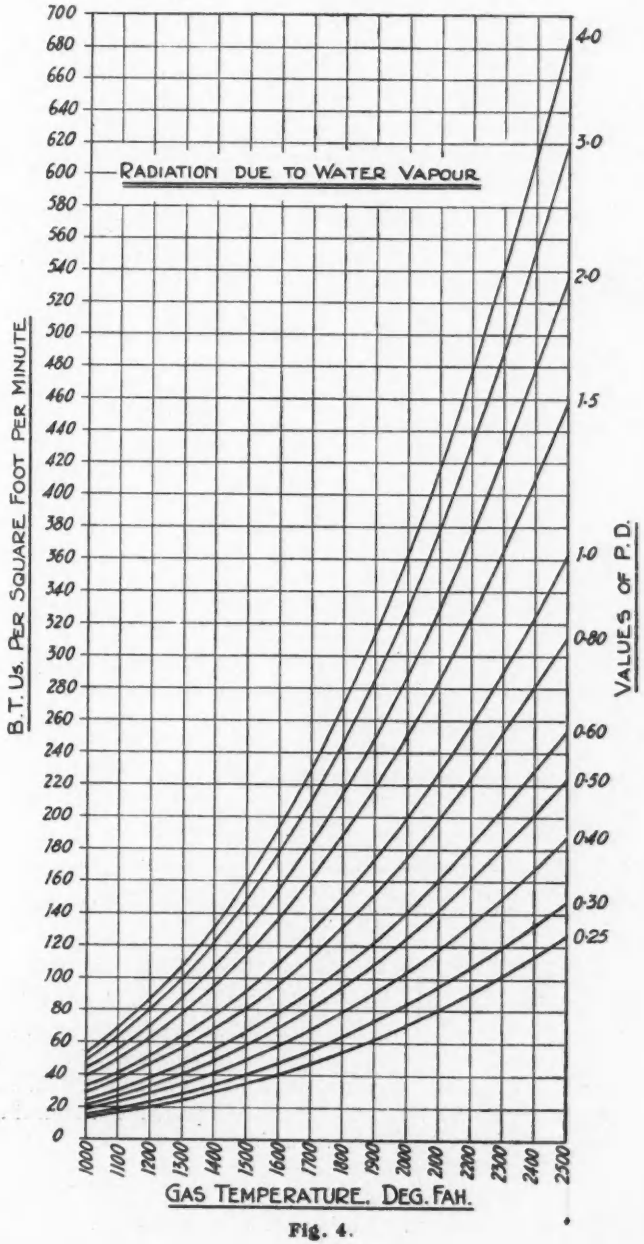

RADIATION DUE TO WATER VAPOUR
B.T.Us. PER SQUARE FOOT PER MINUTE
VALUES OF P.D.
GAS TEMPERATURE. DEG. FAH.
700
680
660
640
620
600
580
560
540
520
500
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
4·0
3·0
2·0
1·5
1·0
0·80
0·60
0·50
0·40
0·30
0·25
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300
2400
2500

Fig. 4.

C

Hottel has shown that of the heat radiated by the coal particles per square foot of area a definite fraction reaches the firebrick lining per square foot of area, which is given by

$$F = \{1 - e^{-NaD}\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

The meaning of the symbols is given in Appendix II. When the formula is applied to portions of the lining near either end of the combustion zone a reduction has to be made, since radiation is received from a smaller number of particles.

(33) To use equation (2) the value of NaD is first obtained. The coal particles are treated as spherical, and since the volume of a sphere is $\frac{\pi d^3}{6}$, it is easily shown that the number of coal particles per pound is

$$Np = \frac{6 \times 1728 \times 10^{12}}{\pi d^3 \phi \times 62.4} = \frac{A}{d^3} \text{ where } \log A = 13.6095.$$

If $d = 7$ units, $Np = 118{,}700{,}000{,}000$.

Since the coal particles are assumed to be uniformly distributed in the combustion zone it follows that

$$N = \frac{Np}{Vp}.$$

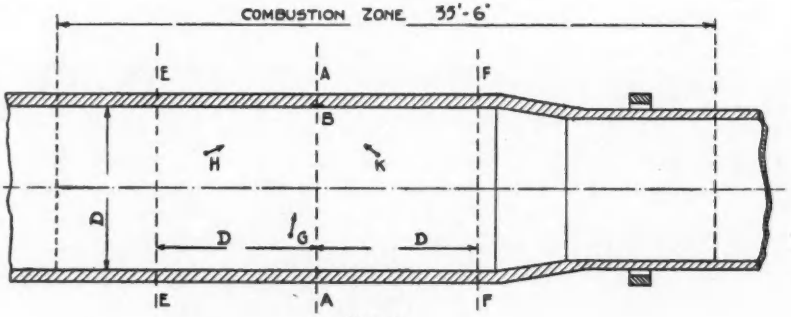


Fig. 5.

(34) The value of a is readily seen to be

$$a = \frac{\pi}{4} \frac{d^2}{10^8} \times \frac{1}{144} = \frac{d^2}{B} \text{ where } \log B = 10.2634$$

hence $$NaD \text{ (initial value)} = \frac{A}{d^3 Vp} \times \frac{d^2}{B} \times D = \frac{2219 \times D}{d \times Vp}.$$

As the particle moves along the combustion zone its diameter is reduced; this affects the value of a, but not the value of N, except in so far as Vp changes. The diameter at any instant is proportional to the cube root of the volume and the corresponding value of a is proportional to the square of that diameter; therefore since b denotes the percentage of the coke particle not burned the value of NaD at any point in the combustion zone is

$$NaD = \frac{2219 \times D}{d \times Vp} \left(\frac{b}{100}\right)^{\frac{2}{3}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

the appropriate values of b and Vp being put into the formula.

(35) As an example we may calculate the values of NaD and F near the centre of the combustion zone, that is at section AA on *Fig.* 5. At this point the $CaCO_3$ is half decomposed, and about 41 per cent. of the average coal particle is not consumed. The mixed gas and air temperature was 2,090 deg. F. and the value of Vp was 938. Taking D at 8.5 ft., the value of NaD, by formula (3), becomes

$$NaD = \frac{2219 \times 8.5}{7 \times 938}\left(\frac{41}{100}\right)^{\frac{1}{3}} = 1.58$$

(36) Returning to formula (2) in para. (32) we have now for the fraction of the coal particle radiation which reaches the kiln lining at the cross section considered

$$F = 1 - e^{-1.58}$$

This equation is not difficult to solve, but since it is often used Table No. V has been prepared. It gives values of F for the values of NaD which are likely to occur in practice. From the Table the value of F is seen to be 0.793.

(37) Taking the temperature of the coal particles to be 2,450 deg. F. and the lining temperature at the section considered 2,230 deg. F., the total radiation which the lining can receive or emit, expressed in B.T.U.'s per square foot per minute, is obtained from Table I as follows:

2,450 deg.	2,070
2,230 deg.	1,512
	558

If, however, we assume that the coal particles can only emit up to 95 per cent. of black body radiation, and that the firebrick lining can only absorb up to 90 per cent. of black body radiation, the actual heat supply to the lining expressed in B.T.U.'s per square foot per minute is reduced approximately to

$$0.95 \times 0.90 \times 0.793 \times 558 = 378.$$

It is possible that formula (2) for various reasons somewhat overestimates the value of F.

Heat Transfer by Convection.

(38) The gases flowing through the kiln give up a proportion of their heat to the lining, material, or chains, by moving contact or convection, the internal

TABLE V.

RADIATION FROM PULVERISED COAL.

NaD	$1 - e^{-NaD}$	NaD	$1 - e^{-NaD}$	NaD	$1 - e^{-NaD}$
0.1	0.095	1.1	0.667	2.2	0.889
0.2	0.181	1.2	0.699	2.4	0.910
0.3	0.259	1.3	0.727	2.6	0.926
0.4	0.329	1.4	0.753	2.8	0.939
0.5	0.394	1.5	0.777	3.0	0.950
0.6	0.452	1.6	0.798	3.2	0.959
0.7	0.504	1.7	0.817	3.4	0.967
0.8	0.550	1.8	0.835	3.6	0.973
0.9	0.593	1.9	0.850	3.8	0.978
1.0	0.632	2.0	0.865	4.0	0.982

diameter of the tubes concerned in the kiln or cooler ranging from 4 to 12 ft. Unfortunately, however, the experiments so far made on this subject relate to tubes less than 6 in. in diameter. The Fuel Research Board has recently examined the published results of a large number of these experiments, and has stated the factors on which it thinks the rate of heat transfer by convection should depend. For air or flue gases flowing through the interior of a tube the formula derived reduces to

$$H_c = \frac{19.7 \times C^{0.8} \times K^{0.2} \times V^{0.8}}{D^{0.2}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

where

H_c = rate of heat transfer in B.T.U.'s per square foot per hour per deg. F. temperature difference.

C = specific heat of the gas, expressed in B.T.U.'s per cubic foot per deg. F. at atmospheric pressure.

K = conductivity of the gas expressed in B.T.U.'s per square foot per hour per deg. F. per foot thick.

V = gas velocity in feet per second.

D = internal diameter of tube in feet.

(39) The quantities C and K relate to the thin layer of the gas which is in contact with the surface, and their values are estimated at the mean temperature of the gas and surface.

Formula No. (4) may be used by taking suitable values of C and K from published tables, but it is apparent that the product $A = 19.7 \times C^{0.8} \times K^{0.2}$ can be worked out and tabulated for a suitable range of temperatures. The formula then becomes

$$H_c = \frac{A \times V^{0.8}}{D^{0.2}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

Values of A are given in Table VI, as well as values of $V^{0.8}$, and $D^{0.2}$ corresponding to the values of V and D which are likely to occur in practice. The values of C and K given in the Table relate to air, but the same figures may be used for flue gases without serious error.

(4.) Formula (5) is probably correct under suitable conditions for tubes up to one foot in diameter, but for larger sizes there is reason to think that H_c may reach a steady value for all tubes. In these articles the steady value of H_c is assumed to occur at $D = 5$.

EXAMPLE.—In a rotary kiln the gas velocity is 25 feet per second, the gas temperature is 1,400 deg. F., and the material temperature 200 deg. F. The kiln is 8 ft. in diameter inside the lining. What is the value of H_c?

The mean temperature of the gas and material is 800 deg. F., hence, taking the limiting diameter at 5 ft., we have from Table No. VI

$$H_c = \frac{0.191 \times 13.1}{1.38} = 1.81$$

Calculated to a diameter of 8 ft. the value of H_c would have been 1.65.

APPENDIX No. I.

A PROBLEM IN RADIATION.

(41) Referring again to *Fig.* 3, suppose that neither plate is a full radiator but that plate *A* can either radiate or absorb up to 80 per cent. of the black body radiation which corresponds to its temperature, and plate *B* up to 70 per cent. The plates are supposed to be maintained at temperatures of 1,800 deg. F. and 600 deg. F. as before.

Each plate is considered in turn; the assumptions first made are not complete, but the correct result is finally evolved. All heat quantities are given in B.T.U.'s per square foot per minute.

By Table I—

	A radiates to *B* 0.8 × 753.5	602.8
Of this quantity		
	B can absorb 0.7 × 602.8	422.0
	B reflects back to *A* 0.3 × 602.8	180.8
	B radiates to *A* 0.7 × 36.5	25.6
(*a*)	Hence *B* gains 422.0 — 25.6	396.4
	and *B* sends back to *A* 180.8 + 25.6	206.4
	A now absorbs 0.8 × 206.4	165.1
	A reflects back to *B* 0.2 × 206.4	41.3
	A radiates to *B*, as before	602.8
Of these quantities		
	B can absorb 0.7 (41.3 + 602.8)	450.9
	B reflects back to *A* 0.3 (41.3 + 602.8)	193.2
	B radiates to *A*, as before	25.6
(*b*)	Hence *B* gains 450.9 — 25.6	425.3
	and *B* sends back to *A* 193.2 + 25.6	218.8
	A now absorbs 0.8 × 218.8	175.0
	A reflects back to *B* 0.2 × 218.8	43.8
	A radiates to *B*, as before	602.8
Of the above quantities		
	B can absorb 0.7 (43.8 + 602.8)	452.6
	B reflects back to *A* 0.3 (43.8 + 602.8)	194.0
	B radiates to *A*, as before	25.6
(*c*)	Hence *B* gains 452.6 — 25.6	427.0

(42) A comparison of the lines (*a*) (*b*) and (*c*) shows that the steady state is now nearly reached, so that the process is not carried farther. It is seen that under the conditions of the problem *B* received approximately 427 B.T.U.'s per square foot per minute.

If the two plates are assumed to be of the same temperature, the absorbing or radiating powers remaining as before, it can be shown by this method that the radiation escaping from a small hole in either plate would be black body radiation.

TABLE VI.

RELATING TO CONVECTION FORMULA.

Temperature Fahr.	$A = 19.7 \times C^{0.8} \times K^{0.2}$	Temperature Fahr.	$A = 19.7 \times C^{0.8} \times K^{0.2}$	V Feet per Second.	$V^{0.8}$	V Feet per Second.	$V^{0.8}$	D Feet.	$D^{0.2}$
60	0.348	1,300	0.160	10	6.31	23	12.3	0.10	0.63
100	0.335	1,400	0.155	11	6.81	24	12.7	0.25	0.73
200	0.302	1,500	0.150	12	7.30	25	13.1	0.50	0.87
300	0.274	1,600	0.146	13	7.78	26	13.6	0.75	0.94
400	0.249	1,700	0.142	14	8.26	27	14.0	1.0	1.00
500	0.229	1,800	0.138	15	8.73	28	14.4	2.0	1.15
600	0.214	1,900	0.135	16	9.19	29	14.8	3.0	1.25
700	0.202	2,000	0.132	17	9.65	30	15.2	4.0	1.32
800	0.191	2,100	0.128	18	10.1	31	15.6	5.0	1.38
900	0.184	2,200	0.126	19	10.5	32	16.0	6.0	1.43
1,000	0.177	2,300	0.123	20	11.0	33	16.4	7.0	1.48
1,100	0.171	2,400	0.120	21	11.4	34	16.8	8.0	1.52
1,200	0.165	2,500	0.118	22	11.9	35	17.2	10.0	1.59

APPENDIX No. II.

RADIATION FROM THE PARTICLES OF PULVERISED COAL.

(43) LIST OF SYMBOLS.

e = 2.7183

d = particle diameter as ground, in units of $\frac{1}{10000}$ in.

ϕ = specific gravity of coal taken at 1.3.

Np = number of coal particles per pound.

N = number of coal or coke particles per cubic foot in the combustion zone.

Vp = volume of products of combustion and excess air per pound of coal in the combustion zone at the appropriate temperature.

a = area of each coke particle in cross section in square feet.

D = kiln diameter inside lining in feet.

F = fraction of coke particle radiation per unit area which reaches the kiln lining per unit area.

b = percentage of coke particle not burned at any instant.

"Sirocco" High Pressure Fans.—Messrs. Davidson & Co., Ltd., of Belfast, have issued a new publication (No. S.F. 26) dealing with "Sirocco" fans for moderate and high pressures. It includes some interesting examples of recent installations and contains detailed information concerning duties, weights, and dimensions for the wide range of sizes listed. In addition, numerous tables assist in determining the most suitable "Sirocco" fan equipment for use under diverse operating conditions. Copies of this useful publication will be sent on application to those interested.

INTERNATIONAL DICTIONARY OF CEMENT.

ARRANGED BY DR. C. R. PLATZMAN, WITH COLLABORATORS IN ENGLAND, FRANCE, AND SPAIN.

[A]

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
accelerated soundness test	épreuve accélérée de stabilité de volume	beschleunigte Raumbeständigkeitsprüfung	ensayo acelerado de inalterabilidad de volumen
acetylene welding plant	équipement de soudure acetylènique	Azetylenschweissanlage	instalación de soldadura oxi-acetilénica
adherence	collage au garnissage	Anbacken, das	adherencia al revestemiento
adhesion	adhérence	Haftfestigkeit	adherencia
aggregate	agrégat	Zuschlagstoff	materia añadida
air agitation	agitation par l'air	Luftrührung	agitación por aire
air gap	entrefer	Luftspalt	entrehierro
air moisture	humidité de l'air	Luftfeuchtigkeit	humedad del aire
air separator	séparateur à air	Windsichter	separador de aire
air separation	séparation par l'air	Windsichtung	separación por aire
alloy	alliage	Legierung	aleación
alternating curing	conservation alternatif	Wechsellagerung	conservación alternada
alternating current	courant alternatif	Wechselstrom	corriente alterna
alumina	alumine	Tonerde	alúmina
aluminous cement	ciment alumineux	Tonerdezement	cement aluminoso
amorphous	amorphe	amorph	amorfo
anemometer	anémomètre	Windmesser	anemómetro
angle iron	cornière	Winkeleisen	hierro angular
angle ring	cercle en cornière	Winkelring	anillo de hierro angular
anneal, to	recuire	ausglühen	recocer
anthracite coal	anthracite	Anthrazitkohle	antracita
apron feeder	table d'alimentation	Telleraufgabe	mesa de alimentación
argillaceous	argileux	tonhaltig	arcilloso
ash	cendre	Asche	ceniza
average	moyen	Durchschnitt, Mittel	promedio

[B]

ball mill	broyeur à boulets	Kugelmühle	molino de bolas
band conveyor	convoyeur à bande	Bandtransporteur	transportador de cinta
barrel	baril	Fass	barril
barrel packing machine	embarilleuse	Fasspackmaschine	envasadora
basic	basique	basisch	básico
belt drive	commande par courroie	Riemenantrieb	transmisión par correa
belt conveyor	transporteur à courroie	Bandtransporteur	transportador de correa
bending strength	résistance à la flexion	Biegefestigkeit	resistencia a la flexión
bending stress	effort de flexion	Biegespannung	esfuerzo de flexión
bevel drive	engrenage conique	Kegelradantrieb	engranaje conico
bin	silo	Behälter	silo
blast furnace	haut fourneau	Hochofen	alto horno
blast-furnace cement	ciment de laitier	Hochofenzement	cemento de altos hornos
blast-furnace slag	laitier de haut fourneau	Hochofenschlacke	escoria de altos hornos
blasting	abattage à la poudre	Sprengung	voladura
boiler	chaudière	Kessel	caldera
boiling test	épreuve d'ébullition	Kochprobe	ensayo a la ebullición

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
bolt	boulon	Bolzen	perno
break	rupture	Knick, Riss	inflexión asodadura
breeze concrete	béton de mâchefer	Schlackenbeton	hermigón de escorias
brickwork	maçonnerie	Ziegelmauerwerk	cámara de ladrillo
Brinell hardness	dureté Brinell	Brinellhärte	dureza Brinell
briquette	brique	Ziegel	briqueta
brittleness	fragilité	Brüchigkeit	fragilidad
bucket	godet	Becher	cangilón
bunker	soute	Bunker	carbonera
burette	burette	Bürette	bureta
burn, to	cuire	brennen	cocer, arder
burner pipe	tuyau du brûleur	Brennrohr	tuberia del mechero
burner's platform	plateforme de chauffage	Brennplattform	plataforma del calcinador
burning zone	zóne de cuisson	Sinterzone	zona de clinkerización

[C]

cableway	transporteur aérien	Seilbahn	transportador aéreo de cable
calcareous	calcaire	kalkhaltig	calcáreo
calcium hydroxide	hydrate de chaux	Kalkhydrat	hidrato de cal
calibrate, to	graduer, classer	kalibrieren	calibrar
calorific value	pouvoir calorifique	Heizwert	potencia calorífica
capillary tube	tube capillaire	Kapillarrohr	tubo capilar
carbon monoxide	oxyde de carbone	Kohlenoxyd	protóxido de carbono
carbon steel	acier au carbone	Kohlenstoffstahl	acero al carbono
carbonic acid	acide carbonique	Kohlensäure	anhídrido carbónico
casting	moulage	Gehäuse	pieza de fundición
cast iron	fonte	Gusseisen	fundición de hierro
cast steel grating	grille en acier fondu	Gusstahlgreting	parrilla de acero fundido
caterpillar track	chenille	Raupenrad	rueda de oruga
cement manufacture	fabrication de ciment	Zementherstellung	fabricación del cemento
cement testing laboratory	laboratoire de cimenterie	Zementprüflaboratorium	laboratorio de ensayo de cemento
central drive	commande par le tourillon	Zentralantrieb	accionamiento por muñón central
centrifugal force	force centrifuge	Zentrifugalkraft	fuerza centrífuga
centrifugal separator	séparateur centrifuge	Zentrifugalabscheider	separador centrífugo
chain	chaîne	Kette	cadena
chain discharge	vidange au moyen d'un système à chaîne	Kettenentleerung	descarga de cadena
chain drive	commande par chaîne	Kettenantrieb	transmisión por cadena
chalk	craie	Kreide	marga
chimney	cheminée	Schornstein	chimenea
chute	dévaloir	Schütte	tolva
circular kiln	four circulaire	Ringofen	horno circular
clay	argile	Ton	arcilla
clean, to	nettoyer	reinigen	limpiar
clearance	jeu	Toleranz	huelgo
clinker concrete	béton de clinker	Klinkerbeton	hormigón de clinker
clinker grinding	mouture du clinker	Klinkermahlung	molturación del clinker
clinker ring	anneau de clinker	Klinkerring	anillo de clinker
clutch	appareil d'embrayage	Kupplung	embrague
coal ash	cendre de charbon	Kohlenasche	ceniza del carbon
coal feed	alimentation en charbon	Kohlenzufuhr	alimentacion de carbón
coarse	grosseur	grob	grueso
coefficient of thermal expansion	coéfficient de dilatation thermique	Wärmeausdehnungskoeffizient	coeficiente de dilatación térmica

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
coke oven gas	gaz de fours à coke	Koksofengas	gas del horno de coke
cold water test	essai à eau froide	Kaltwasserprobe	ensayo al agua fria
collecting electrode	électrode collectrice	Abscheidungselektrode	electrodo captador
combined storage	conservation combiné	kombinierte Lagerung	conservación combinada
combustion	combustion	Verbrennung	combustión
common lime	chaux grasse	Luftkalk	cal grasa
commutator	commutateur	Umschalter	commutador
composition	composition	Zusammensetzung	composición
compound	substance	Bestandteil	compuesto
compound condensing steam engine	machine à vapeur compound à condensation	Verbunddampfmaschine m. Kondensation	máquina compound de vapor con condensación
compound mill	tube broyeur compound	Verbundmühle	molino combinado
compressed air	air comprimé	Druckluft	aire comprimido
compressed air drill	perforatrice sur air primé	Pressluftbohrung	perforador de aire comprimido
compressed air hammer drill	perforatrice à percussion à air comprimé	Druckluftbohrhammer	martillo perforador neumático
compressed-pat kiln test	épreuve sur galette comprimée et etuvée	Presskuchendarrprobe	ensayo de galleta comprimida
compression strength	résistance à la compression	Druckfestigkeit	resistencia a la compresión
compression testing machine	machine d'essai de résistance à la compression	Druckfestigkeitsprüfmaschine	máquina para el ensayo de la resistencia a la compresión
compressive stress	effort de compression	Druckspannung	esfuerzo de compresión
concrete	béton	Beton	hormigón
conductivity	conductibilité	Leitfähigkeit	conductividad
continuous current	courant continu	Gleichstrom	corriente continua
continuous working kiln	four continu	Ofen mit ständigem Betrieb	horno de marcha continua
contract, to	se contracter	schwinden	contraerse
cooler	refroidisseur	Kühler, Kühlrohr	enfriador
correction tank	bassin pour la mise au point de la composition	Korrektionstank	depósito de corrección de la mezcla
cotton	coton	Baumwolle	algodón
counter	compteur	Zählvorrichtung	contador
counter-flow	contre-courant	Gegenstrom	contra-corriente
cover-glass	couvercle en verre	Deckglas	cristal cubreobjeto
crack, craze	fendillement	Riss, Sprung	raja, grieta
crack due to contraction	fendillement dû au retrait	Schwindriss	grieta debida a la contracción
crack due to expansion	fissure due à l'expansion	Treibriss	grieta debida a la dilatación
crane	grue	Kran	grúa
cross section	section transversale	Querschnitt	sección transversal
crucible	creuset	Tiegel	crisol
crucible steel	acier au creuset	Tiegelstahl	acero al crisol
crumble, to	tomber en fragments	zerbröckeln	desmenuzarse
crusher	concasseur	Brecher	trituradora
cube	cube	Würfel	cubo
cubic centimetre	centimètre cube	Kubikzentimeter	centímetro cúbico
cure, to	garder	lagern	conservar
cutting tool	outil tranchant	Werkzeugschneide	herramienta de filo
cyclone	cyclone	Zyklon	ciclón
cylinder	cylindre	Zylinder	cilindro

[D]

ENGLISH.	FRENCH.	GERMAN.	SPANISH.
damp atmosphere	air humide	feuchte Luft	aire húmedo
decomposition	décomposition	Zersetzung	descomposición
definition	définition	Begriffserklärung	definición
deflection	flèche	Durchbiegung	flecha
deformation	déformation	Formänderung	deformación
degree	degré	Grad	grado
dehydration	déshydratation	Wasserabspaltung, Entwässerung	deshidratación
density	densité	Dichte	densidad
deposit	dépôt	Lager, Vorkommen	yacimiento
depth	profondeur	Höhe, Tiefe	profundidad
design	projet	Entwurf, Bauart	módulo
dial	cadran	Zifferblatt	cuádrante
diameter	diamètre	Durchmesser	diámetro
disc crusher	concasseur à cône oscillant	Scheibenbrecher	trituradora de discos
disc filter	filtre à disque	Scheibenfilter	filtro de discos
discharge electrode	électrode émettrice	Entladungs-, Abscheidungselektrode	electrodo de descarga
discharge lock	sas de vidange	Entleerungsschleuse	compuerta de descarga
disengagement	débrayage	Ausschaltung	desembrague
disintegrate, to	désagréger	zerrieseln	desintegrar
dispatch	expédition	Verladung; Verladen, das	despacho de mercancías
distortion	distortion	Verkrümmung	distorsíon
double refracting	double réfraction	doppelbrechend	birrefringencia
dragline excavator	excavateur à cables	Bagger mit Leitseil, Schrapper	excavadora o draga de cable
drier	séchoir	Trockner	secador
drill	perforatrice	Gesteinsbohrer	taladro perforador
drilling machine	perceuse	Bohrmaschine	máquina perforadora
drum type controller	contrôleur du type à tambour	Walzenumschalter	controller de tipo de tambor
drum type separator	séparateur à tambour	Trommelabscheider	separador de tipo de tambor
drying drum	séchoir rotatif	Trockentrommel	secador rotatorio
dry process	procédé sec	Trockenverfahren	vía seca
dust	poussière	Staub	polvo
dust-collecting plant	équipement dépoussiéreur	Staubsammlungsanlage	instalación de captación de polvo
dustproof (dust-tight)	impénétrable à la poussière	staubfrei (staubdicht)	herméticamente cerrado al polvo
dynamo	dynamo	Dynamo	dínamo

[E]

earthing	mise à la terre	Erdung	toma de tierra
earth moist	consistance de la terre humide	erdfeucht	consistencia de tierra húmeda
edge crack	fendillement sur le bord	Kantenriss	grieta ó raja en el borde
edge-runner	broyeur à meules	Kollergang	triturador de noria
efflorescence	croûte salée	Ausblühung	costra de sal
electric power	énergie électrique	elektr. Kraft	energia eléctrica
elongation	allongement	Dehnung	alargamiento
elutriator	séparateur	Sichter	levigador
elutriation analysis	analyse par sédimentation	Schlämmanalyse	análisis por levigación
enclosed	enfermé	gekapselt	cerrado
evaporation	évaporation	Verdampfung, Verdunstung	evaporación

(*To be Continued*).

The Hydration of Tricalcium Aluminate.

A JOINT report of the U.S.A. Calcium Chloride Association and the Ohio State Engineering Experiment Station on their investigation of the action of calcium chloride on Portland cement, was given recently as a paper read by Mr. W. D. Foster before the American Concrete Institute.

The hydration of tricalcium aluminate is important, states the report, because it is apparently one of the minerals responsible for the initial set of Portland cement. Rankin and Wright first proved its presence in Portland cement by their phase rule studies on the CaO-Al_2O_3-SiO_2 system. More recently Brownmiller and Bogue have shown its presence in commercial Portland cements by the use of X-rays. Klein and Phillips and later Wells have studied the hydration of tricalcium aluminate and agree that the reaction as a whole is the simple addition of water to the anhydrous tricalcium aluminate as follows:

$$3CaO.Al_2O_3 + nH_2O = 3CaO.Al_2O_3.nH_2O$$

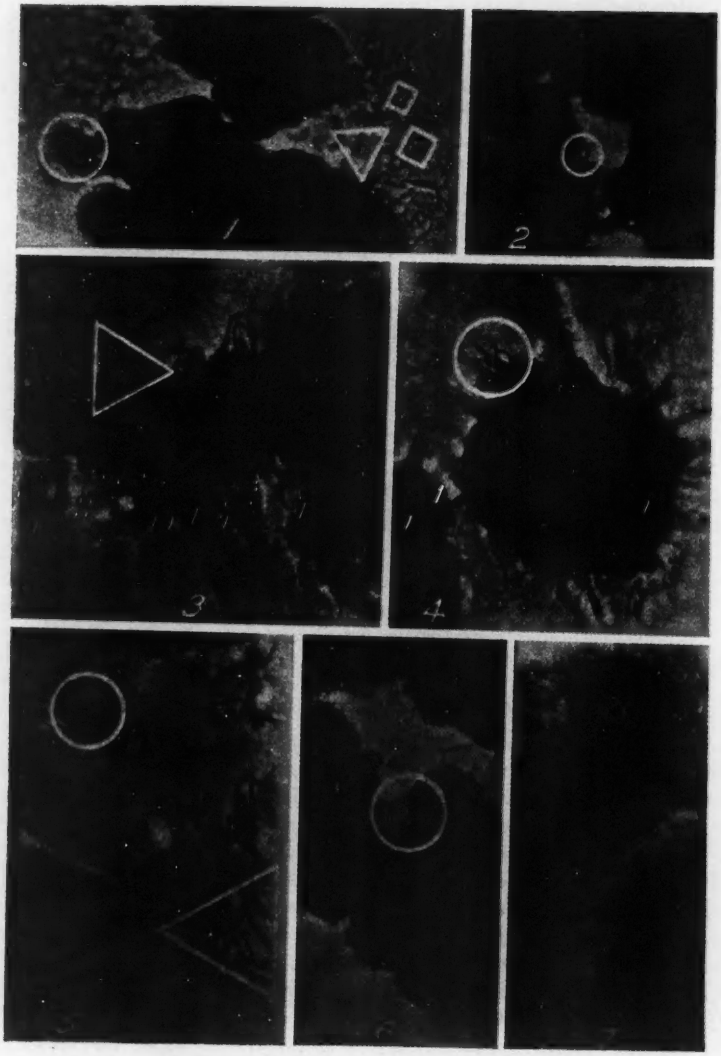
Thorvaldson has studied the products of this reaction and reports four hydrates, $3CaO.Al_2O_3.6H_2O$, $3CaO.Al_2O_3.8H_2O$, $3CaO.Al_2O_3.10.5H_2O$, $3CaO.Al_2O_3.12H_2O$. The hexahydrate is isometric and is formed at relatively higher temperatures that the others. The other three hydrates are hexagonal and for practical purposes indistinguishable.

The purpose of this paper is twofold: first, to study the character and the approximate rate of hydration of tricalcium aluminate in water and various salt solutions, principally calcium chloride and sulphate; second, to determine the rate of hydration of tricalcium aluminate in water alone and with calcium chloride and sulphate admixed. The character of hydration was observed microscopically and the products of hydration identified by their optical properties. Photomicrographs were taken frequently for illustration. For an accurate determination of the rate of hydration the Hubbell method was chosen.

The Character of Hydration of Tricalcium Aluminate.

When tricalcium aluminate is added to water it passes into solution with dissociation, giving, among other things, calcium ions. The calcium and alumina in solution then recombine as the tricalcium aluminate hydrate and this precipitates. Calcium ions already present in solution from a soluble calcium salt should retard the formation of calcium ions from the tricalcium aluminate and thus retard its hydration. Dilute solutions of all soluble calcium salts available, which included the calcium chloride, sulphate, acetate, bromide, chlorate, chromate, hydroxide, iodide, lactate, nitrate, nitrite and permanganate, were tested. They all retarded the hydration of the tricalcium aluminate.

The hydrate of tricalcium aluminate is amorphous at first and later crystallises. In water this crystallisation of the amorphous gel-like hydrate takes place almost immediately. Fig. 1 shows tricalcium aluminate in water for ten minutes. There is a border of needle-like crystals around the grains (in circle) and much amorphous (in triangle) and crystalline hydrated material (hexagonal plates in squares) a short distance from the grains.



Figs. 1-7.—Magnification 359 diameters.

Dilute solutions of calcium salts, besides retarding hydration, strongly inhibit crystallisation of the amorphous hydrated material. Fig. 2 shows tricalcium aluminate in a saturated gypsum solution for ten minutes. The hydrate is forming slowly as globules of amorphous material on the surface of the grains (in circle). Similar conditions were observed when a saturated calcium hydroxide solution and a very dilute calcium chloride of approximately the same normality as the gypsum and calcium hydroxide solutions were used.

Proportions of 2, 4 and 8 per cent. $CaCl_2$ solutions acted similarly in inhibiting crystallisation. The amount of hydrated material at ten minutes, or the rate of hydration, increased with the concentration of the calcium chloride until the rate of hydration in the 8 per cent. solution was approximately the same as in water alone. A nearly saturated calcium chloride solution, about 37.5 per cent. $CaCl_2$, acted still more rapidly. The tricalcium aluminate was rapidly breaking down to an amorphous mass. At the end of one hour it was practically completely broken down to an amorphous homogeneous mass, and hydration was complete.

Tricalcium aluminate was also hydrated in 2, 4, and 8 per cent. $CaCl_2$ solutions saturated with gypsum, and in similar calcium chloride solutions carrying gypsum suspended in them. No appreciable difference was noted between the effect of these and the solutions without gypsum. Crystals of calcium sulpho-aluminate had not appeared at ten minutes.

When something is present to delay crystallisation of the amorphous tricalcium aluminate hydrate it frequently happens that the grains of tricalcium aluminate can be seen glued together by a gel forming between them. This gluing together will give a stronger bond than that resulting from the interlacing of crystals, and is more to be desired in the setting of Portland cement than the interlacing crystal type of bond.

After 24 hours in water tricalcium aluminate shows an abundance of crystalline hydrated material (Fig. 3). Sometimes, instead of plates as shown in the figure, a thick border of fine needles was formed.

Tricalcium aluminate in a saturated solution of gypsum shows large ragged crystals of the hydrate (Fig. 4); nothing resembling the sulpho-aluminate is present. If an excess of gypsum is present (Fig. 5), the calcium sulpho-aluminate can be seen bordering the grains and in detached spherulitic clusters (in circle). The unevenly distributed broader and longer crystals (in triangle) are the excess gypsum. The use of excess gypsum has ensured the conversion of the hydrated material to the calcium sulpho-aluminate.

With either a saturated calcium hydroxide solution or a calcium chloride solution of approximately equivalent normality, the hydrate appears as fewer and much smaller crystals. These solutions apparently still inhibit crystal growth at 24 hours. Fig. 6, for the purposes of reproduction, illustrates this, though it is really a picture of the action of 4 per cent. $CaCl_2$ solution saturated with gypsum. Nothing was seen to indicate the formation of a tetracalcium aluminate hydrate with a solution of calcium hydroxide or an excess of calcium hydroxide present.

Tricalcium aluminate in 2 per cent. $CaCl_2$ solution for 24 hours is bordered with fine crystals, very similar to Fig. 6. In 4 per cent. $CaCl_2$ solution, the hydrated material is amorphous at 24 hours but soon crystallises. Tricalcium aluminate hydrated in 2, 4 and 8 per cent. $CaCl_2$ solutions saturated with gypsum is very similar to the calcium chloride solution (Fig. 6). In the 8 per cent. $CaCl_2$ solution saturated with gypsum the two salts, apparently working together, have caused a breaking down of the tricalcium aluminate leaving well-defined nuclei embedded in a mass of amorphous material. This had not appreciably crystallised at nine days.

When tricalcium aluminate is hydrated for 24 hours in 2, 4 and 8 per cent. $CaCl_2$ solutions carrying excess gypsum in suspension, it is broken down apparently by the combined action of the two. With 2 per cent. $CaCl_2$ solution and excess gypsum there are prominent nuclei and a small amount of amorphous material. With 8 per cent. $CaCl_2$ solution plus excess gypsum the grains are practically completely broken down with almost no evidence of nuclei and with heavy amorphous hydrated material. The 4 per cent. $CaCl_2$ solution with excess gypsum is between the extremes and is illustrated in Fig. 7. The amorphous material in these did not crystallise appreciably during several weeks of observation.

These experiments show calcium chloride and gypsum to have an additive effect in retarding the crystallisation of the material resulting from the hydration of the tricalcium aluminate. The apparent greater effectiveness of calcium chloride than gypsum in inhibiting crystallisation of the hydrated tricalcium aluminate may be due only to the greater solubility of the calcium chloride, as at the same concentration the action is nearly identical.

If calcium chloride is used integrally in Portland cement there will be approximately a 4 per cent. $CaCl_2$ solution with excess gypsum. Tricalcium aluminate alone in such a solution would be broken down as in Fig. 7. Whether or not the same thing would happen in Portland cement would have to be learned by further study.

Rate of Hydration of Tricalcium Aluminate.

The rate of hydration of tricalcium aluminate has been determined by the Hubbell method. Five identical trials were made up for each different set of conditions under which the tricalcium aluminate was hydrated. At each time at which hydration was determined, three of the five trials were sampled. Two different fields were counted on each, counting the high and low index particles in quadrants one and three in one, and quadrants two and four in the other. Counting was stopped in each quadrant when a total of about 75 particles had been counted. A total of about 40,000 particles was counted in order to draw the curves shown.

Tricalcium aluminate was made according to the methods used by the Bureau of Standards. It was impossible to eliminate a trace of free lime by repeated firings, but this turned to calcite before any experiments were made. Sized particles were used for this work and for the microscopic work referred to

earlier. These passed a 200-mesh screen but were held on a 300-mesh screen. In all the tests, one gramme of tricalcium aluminate was placed in a 4-in. test tube, 1 c.c. of hydrating solution added, the two mixed, corked, and stored in a constant temperature oven at 35 deg. C. This was a slight excess of hydrating solution, enough to keep the tricalcium aluminate submerged. Tricalcium aluminate was hydrated under seven different conditions: in plain water; in 2, 4 and 8 per cent. $CaCl_2$ solutions; in plain water with 2 and 10 per cent. gypsum added; and in 4 per cent. $CaCl_2$ solution with 2 per cent. gypsum added. Samples were taken at 1, 3, 6, 12, 24 and 48 hours, dried, ground fine, and number of particles above and below 1.67 counted. Fig. 8 shows the rate of hydration of tricalcium aluminate in plain water and in 2, 4 and 8 per cent. $CaCl_2$ solutions. The time is plotted on a logarithmic scale which allows one or more straight lines, fitted to the points by the method of least squares, to be drawn to show the rate of hydration, and incidentally more evenly distributes

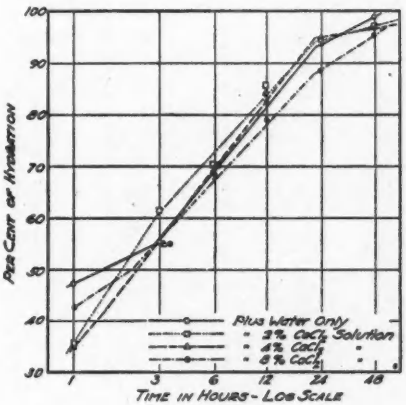


Fig. 8.

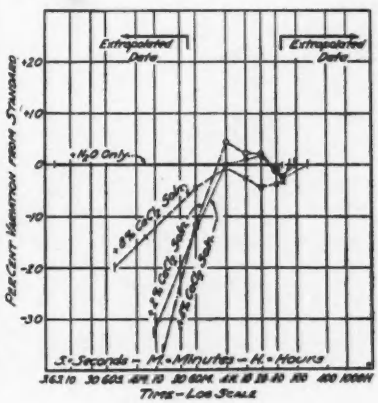


Fig. 9.

on the figure the times at which the amount of hydration was determined. It will be noted that the base line in this figure is at 30 per cent. hydration. The symbols showing the amount of hydration at the various ages are the average of three determinations.

There is no significant difference between these curves except earlier than three hours, where the amount of hydration in the various calcium chloride solutions is less than the amount in plain water. The retardation of hydration is roughly inversely proportionate to the concentration of calcium chloride. To illustrate more easily this early retardation Fig. 9 was drawn. The curve for tricalcium aluminate in plain water is shown as a straight horizontal line. At various ages the plus or minus variation of the amount of hydration in the calcium chloride solutions from the amount in plain water is calculated and plotted. All the curves shown are extrapolated from the known data to cover

the complete time of hydration of the tricalcium aluminate in each solution from 0 to 100 per cent. hydration. The time is again plotted on a logarithmic scale. For convenience the experimentally determined points are not all used; instead, points were interpolated at other ages. Such an interpolation from a curve whose position has been calculated by the method of least squares is fairly accurate.

From the curves on Fig. 9 the retarding effect that calcium chloride has on the hydration of tricalcium aluminate can be more easily seen. The curves for hydration in the calcium chloride solutions are much below the curve for the hydration in plain water at the early ages, and do not meet it until at about

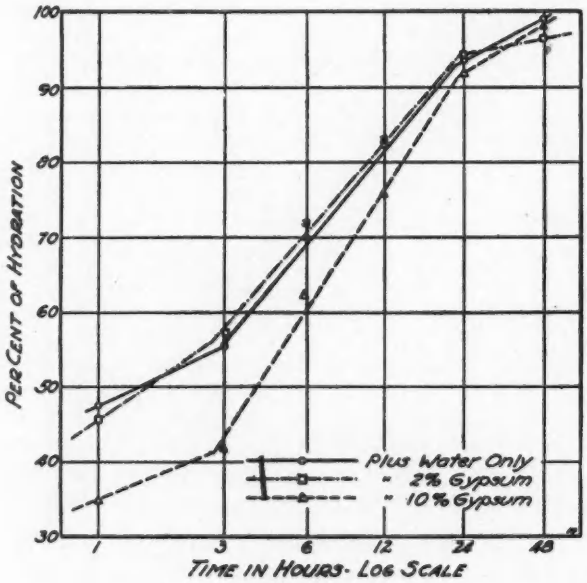


Fig. 10.

three or four hours. From here to the finish of hydration there is no significant difference. The amount of retardation at the early ages is apparently inversely proportionate to the concentration of the calcium chloride. With such large extrapolations there is a large degree of uncertainty, and while the 8 per cent. $CaCl_2$ is probably a poorer retarder than the other two concentrations, quantitative comparison of the 2 and 4 per cent. $CaCl_2$ solutions is not justified. These curves also seem to show that calcium chloride is effective as a retarder for the first several hours, but after this its effectiveness practically ceases. This is probably due to the withdrawal of calcium chloride from the solution to form a calcium chloraluminate with the tricalcium aluminate.

Fig. 10 compares the rate of hydration of tricalcium aluminate in plain water with that of tricalcium aluminate to which 2 and 10 per cent. gypsum has been added. About 2 per cent. of gypsum is added to Portland cement as a retarder, so a similar amount was used with one batch of tricalcium aluminate. As tricalcium aluminate at its maximum will be about 20 per cent. of the Portland cement, the amount of gypsum added is 10 per cent. of this ; so a second batch was used containing 10 per cent. gypsum. Fig. 10 is drawn similarly to Fig. 8, and its previous description will apply. There is no difference noted on this figure between tricalcium aluminate hydrated in plain water and tricalcium aluminate with 2 per cent. gypsum added. The tricalcium aluminate carrying 10 per cent. gypsum is about 12 per cent. lower at one hour than the tricalcium aluminate without gypsum. This difference gradually disappears until at 24 hours it is practically gone.

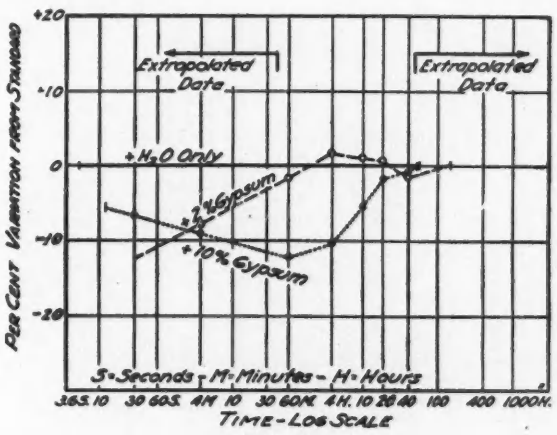


Fig. 11.

To show better the difference in the early hydration, Fig. 11 is drawn on the same plan as Fig. 9. The tricalcium aluminate hydrating in plain water is again used as a standard, and the percentage variation of the tricalcium aluminate plus gypsum mixtures is calculated and plotted. All curves are extrapolated to cover the entire time from 0 to 100 per cent. hydration. The time is plotted on a logarithmic scale as before. From this figure it can be seen that the 2 per cent. gypsum added to the tricalcium aluminate retards the hydration of the tricalcium aluminate at the start, but its effect disappears at about one hour ; also the 10 per cent. gypsum added to the tricalcium aluminate retards its hydration at the start and up to about 24 hours, as has already been noticed. Due to the large amount of extrapolation involved, quantitative comparison of the amount of retardation produced by the two different concentrations of gypsum is not possible. All that can be said is that they are approximately equal. Here again the probable cause of the disappearance of the retarding action of the

gypsum is the combination of the gypsum and the tricalcium aluminate to form a calcium sulpho-aluminate.

Information determined in the same way as to the retarding effect of gypsum mixed with calcium chloride solution shows that, considering only a 4 per cent. $CaCl_2$ solution and a 2 per cent. admixture of gypsum, the best retarder is the 4 per cent. $CaCl_2$ solution, the next best a mixture of the two, and the poorest the 2 per cent. admixture of gypsum. In other words, the retarding action of the gypsum and calcium chloride is not additive in a mixture of the two; instead of this the retarding action of the mixture is nearly an average of the effect of the two salts taken separately.

Calcium chloride and gypsum both retard the hydration of tricalcium aluminate. The effect of the calcium chloride seems to be stronger during the early hydration, during a period corresponding roughly to the time taken for the initial set of the cement. After this its effect disappears. The 10 per cent. of added gypsum apparently does not retard the hydration of the tricalcium aluminate as much at first, but its effect disappears more slowly, lasting to about 24 hours. This more rapid action of the calcium chloride, both as to greater early retarding and quicker disappearance of the retarding action, may be due entirely to the much greater solubility of the calcium chloride.

The retarding action of both the calcium chloride and the gypsum disappears before the hydration of the tricalcium aluminate is completed. This may mean that the calcium chloride and the gypsum disappear as such, combining with the tricalcium aluminate to form complex compounds. Unfortunately, the fact of the disappearance of the retarding effects of the calcium chloride and gypsum was not realised in time to test the hydrating solutions to see if they had actually disappeared. In a previous paper it has been shown that in a solution in which some Portland cement was hydrating, the concentration of calcium chloride dropped. Also, in this series of tests, there is enough tricalcium aluminate present to combine with all the calcium chloride in the 2 and 4 per cent. solutions, if they form the calcium chloraluminate reported in the literature, $3CaO.Al_2O_3.CaCl_2.10H_2O$. It so happens that the 8 per cent. $CaCl_2$ solution, in which the tricalcium aluminate might not be able to take up all the calcium chloride, shows a slight amount of retardation when this effect has disappeared in the other calcium chloride solutions. Whether this is more than a coincidence is not known at present. The tricalcium aluminate also would be able to combine with all the gypsum used in the tests described in this paper if it forms either of the calcium sulpho-aluminates reported in the literature.

New Steel Catalogue.—Messrs. Thos. Firth and John Brown, Ltd., of Atlas and Norfolk Works, Sheffield, 1, the well-known steel manufacturers, have issued an attractive brochure describing the growth of the business through four generations, and giving a great deal of valuable information to steel users. This company has for many years specialised in parts for cement mills and crushers, and readers of this journal are invited to apply for a copy of the brochure; they will find therein much information of interest and value regarding the various steels supplied by the firm.

Chemical Analyses of the Particles of Various Sizes of Ground Cement.

By E. T. CARLSON and P. H. BATES
(OF THE UNITED STATES BUREAU OF STANDARDS).

A RECENT article by Rordam[1] dealing with the question of the effective fineness of cement in relation to its strength-conferring properties is very interesting in one particular feature. This calls attention to the difference in the chemical analyses of the various sizes separated from the cement under investigation. Shimizu[2] also recently called attention to this matter.

The Bureau of Standards has separated five ground Portland cement clinkers from as many mills into five fractions by means of air elutriation. These fractions alone and in several blends will be used in studying the question of fineness in relation to the strength of concrete. A description[3] of the equipment used in making the separations and the major portion of the data being obtained will be presented in a later paper. This paper presents only a discussion of the data resulting from the partial analyses of the fractions of the ground clinker.

Table I presents these partial analyses as well as the analyses of the cement used by Rordam and presented in his paper. It also contains the percentages of tricalcium silicate, dicalcium silicate, $4CaO.Al_2O_3.Fe_2O_3$, and tricalcium aluminate calculated from these analyses. These data reveal in the majority of cases that the compositions of the fractions differ considerably from one another.

The data in the third column show that the finer the fraction the greater the ignition loss. At first thought this might seem to be a resultant of the absorption of moisture from the air during the air elutriation. In making these separations, however, the air admitted to the system was refrigerated until its relative humidity at 80 deg. was below 20 per cent. Further, through a system of recirculating the air during the elutriation, no more than 20 per cent. of outside air was being drawn into the system, the remainder being previously used air. Finally, a calculation of what would be the ignition loss of the ground clinker after the separation, based upon the ignition loss of each fraction and the percentage of each fraction present in the original ground clinker, showed that in the case of clinker A (which showed the largest ignition loss of the finest fractions) slightly less than a total of 0.2 per cent. had been absorbed by all the fractions during the separation.

A little further thought will show that the materials comprising the ignition loss (water and CO_2 largely) should be present to a greater extent in the finer portions of any ground clinker before any size separation might be made. A gram of a fraction from 0 to 7 microns in diameter will have a surface of approxi-

[1] Rordam's, "What is the Essential Flour in Cement?" *Cement and Cement Manufacture*, January, 1933.
[2] Shimizu, Fine Grinding of Cement: *Review of the Twentieth General Meeting of the Association of Japanese Portland Cement Engineers*: Foreign edition, 1931.
[3] The apparatus used was designed by L. A. Wagner of this Bureau, who also made the separations.

TABLE I.

PARTIAL CHEMICAL ANALYSES OF THE CLINKERS AND CALCULATED COMPOSITIONS: ON IGNITION LOSS FREE BASIS.

Clinker.	Fraction Size in Microns.	Ignition Loss.	SO_3.	SiO_2.	CaO.	Fe_2O_3.	Al_2O_3.	3CS.	2CS.	4CAF.	3CA
		%	%	%	%	%	%	%	%	%	%
	Whole	2.4	—	21.0	65.5	3.7	6.9	55.0	19.0	11.3	12.0
	0–7	6.4	0.19	20.3	65.3	3.6	7.5	58.0	14.5	10.9	13.2
	7–22	2.5	—	20.4	65.8	3.5	7.1	60.0	13.0	10.6	13.0
"A"	22–45	1.5	—	21.2	65.5	3.6	7.2	52.0	21.5	10.9	13.0
	45–75	1.1	—	21.1	64.8	3.7	7.4	49.0	23.5	11.3	13.2
	75-(*a*)	0.9	0.11	21.1	64.4	3.7	7.5	47.0	25.0	11.3	13.5
	Whole	1.3	—	22.0	66.2	2.5	6.6	60.0	17.5	7.6	10.9
	0–7	2.8	0.44	22.0	66.2	2.1	6.4	62.5	16.0	6.3	11.4
	7–22	1.2	—	22.3	66.5	2.2	6.5	59.5	19.0	6.9	11.4
"B"	22–45	0.7	—	22.2	66.0	2.6	6.0	63.0	16.0	7.9	9.0
	45–75	0.6	—	21.6	65.6	3.0	6.7	61.0	16.0	9.1	9.8
	75-(*a*)	0.7	0.33	21.2	65.2	3.5	6.9	62.0	14.0	10.6	9.0
	Whole	1.4	—	21.0	65.5	2.3	7.1	56.0	18.0	7.0	14.9
	0–7	4.1	0.69	20.7	65.6	2.3	6.7	61.5	13.0	7.0	13.8
	7–22	1.5	—	21.0	66.0	2.2	6.3	63.0	12.5	6.7	13.0
"C"	22–45	0.8	—	21.6	65.5	2.3	6.6	55.5	20.0	7.0	13.5
	45–75	0.6	—	21.6	65.1	2.4	7.1	49.0	25.0	7.3	14.9
	75-(*a*)	0.5	0.22	21.9	64.5	2.5	7.0	46.0	28.0	7.6	14.3

TABLE I.—(*Continued.*)

PARTIAL CHEMICAL ANALYSES OF THE CLINKERS AND CALCULATED COMPOSITIONS: ON IGNITION LOSS FREE BASIS.

Clinker.	Fraction Size in Microns.	Ignition Loss.	SO_3.	SiO_2.	CaO.	Fe_2O_3.	Al_2O_3.	3CS.	2CS.	4CAF.	3CA.
		%	%	%	%	%	%	%	%	%	%
	Whole	1.2	—	19.6	66.4	2.5	6.9	72.0 *(70.0)	2.0 *(3.0)	7.6	14.1
	0–7	2.2	1.04	19.3	65.9	2.5	6.8	72.0	1.0	7.6	13.8
	7–22	0.9	0.41	20.0	66.0	2.4	6.7	68.0	6.0	7.3	13.8
"D"	22–45	0.7	0.37	20.1	66.9	2.4	6.8	70.0	5.0	7.3	13.8
	45–75	0.6	0.38	19.4	66.8	2.5	7.3	72.0 *(68.5)	1.0 *(4.5)	7.6	15.1
	75-(*a*)	0.3	0.42	19.5	66.5	2.6	7.4	70.0	3.0	7.9	15.1
	Whole	0–7	—	23.8	65.4	5.6	3.5	54.5	27.0	17.0	0.6
	0–7	2.6	0.11	21.0	65.7	7.1	4.2	64.0	12.5	19.8	(*)1.0
	7–22	0.8	—	23.0	66.3	5.4	3.5	64.0	17.5	16.4	0.0
"E"	22–45	0.5	—	24.7	65.6	5.0	3.4	50.5	33.0	15.2	0.5
	45–75	0.4	—	24.8	65.2	5.4	3.3	46.0	36.5	16.4	0.0
	75-(*a*)	0.3	0.12	25.0	65.4	5.8	3.7	38.0	43.0	17.6	0.0
	Whole	—	—	21.9	65.9	2.6	5.8	59.5	18.0	8.0	10.8
	0–10	—	—	21.1	66.5	2.5	6.0	66.5	10.6	7.6	11.6
Rordam	10–25	—	—	22.3	65.9	2.5	5.5	59.0	19.0	7.6	10.3
	25–50	—	—	22.4	65.0	2.6	5.6	56.5	21.5	8.0	10.4
	>50	—	—	22.8	64.2	2.7	6.1	49.0	36.0	8.3	12.8

(*a*) = 200 mesh sieve.

* Figures in parentheses have had allowance made for CaO combined with SO_3.

(*) = $2CaO.Fe_2O_3$.

3CS = $3CaO.SiO_2$. 2CS = $2CaO.SiO_2$. 4CAF = $4CaO.Al_2O_3.Fe_2O_3$. 3CA = $3CaO.Al_2O_3$.

mately 5,000 sq. cm., a gram between 7 and 22 microns a surface of approximately 1,280 sq. cm., and each fraction of larger size will have less surface until a gram of the coarsest fraction in question (75 microns, 200 mesh) has only 160 sq. cm. of surface. Since the water and the carbonic acid would undoubtedly be absorbed to the same depth on the surface of all particles, it can be readily realised how much more ignition loss will be shown by the finer particles of any commercial cement compared with coarser ones.

The analyses and calculated composition of the cement dealt with in Rordam's paper show very conclusively that the fine size is richest in tricalcium silicate and that there is a decrease in this constituent in each coarser size; that the fine particles are leanest in dicalcium silicate, and each coarser size shows an increase in this constituent; and that there is very little difference between the fine and coarse fractions in their content of tricalcium aluminate or $4CaO.Al_2O_3.Fe_2O_3$. The analyses of the five brands separated at the Bureau show the same general trend in the case of clinkers A, C, and E. Clinker D is a high-early-strength Portland cement characterised by rather lower silica content than usual and containing a very small amount of dicalcium silicate. As a consequence this brand could hardly show much variation in the relative amounts of the silicates in any fraction. Clinker B, however, is a normal Portland cement, and why it should show a uniform distribution of the two silicates among the various sized particles cannot be explained at present.

It should be noted also that the difference in chemical composition between the fraction of least-size particles and that of next larger size ones is slight. Indeed, one might conclude there was a tendency for the amount of tricalcium silicate in the finest size to be somewhat less than in the next larger size. The differences indicated, however, are within the experimental error; very slight differences in the analytical results are very much magnified in the calculations of the components—0.1 per cent. decrease in silica accompanied by a like increase in lime content will result in 1 per cent. increase in tricalcium silicate.

The five clinkers do not show any difference in the fractions so far as the relative amounts of the $4CaO.Al_2O_3.Fe_2O_3$ compound and tricalcium aluminate are concerned, again with the possible exception of clinker B. Here there does seem to be an indication that the ternary compound is present to a greater extent in the coarser particles and the tricalcium aluminate in the finer particles.

Although these separations were made with samples of ground clinker and not from samples of ground cement containing the usually added gypsum, the results show that there is a tendency for the calcium sulphate in the clinker (resulting largely from the absorption of sulphur gases from the kiln atmosphere) to be present to a greater extent in the fine fractions.

It is believed that the concentration of the tricalcium silicate in the finer fractions is due to a greater ease of grinding this constituent. The lumps of clinker are a heterogeneous sintered and sometimes fused mass of the several constituents. The fact that the last of these constituents to form is the tricalcium silicate, due to its high temperature of formation from the oxides, would seem to

indicate that generally it would be the most friable. Hence in the course of crushing and grinding it would more readily reduce to a given size than the other components. Since in the usual mill procedure the coarse limit of the grinding fixes the amount of the grinding, it would very likely follow that in attaining this limit the softer particles had been subjected to more attrition than the harder ones.

This work does not indicate that in the air elutriation there has been a segregation of the components of the cement other than that of size. That the finer-size fractions differ in chemical composition from the coarse ones is due to the fact that in the grinding of the clinker there has been a greater size reduction of some of the components than of others. Therefore, in the commercial cements, it is likely that different sizes will vary in composition. Shimizu, to whom reference has already been made, separated the fractions he obtained by means of sieves of various dimensions and thus secured three fractions, in which, from the fine to the coarse, the hydraulic modulus ranged from 2.25 to 2.17 and the silica modulus from 2.75 to 2.63.

Conclusions.

A separation of the particles of ground clinker from five different sources into five sizes shows that in commercial cements

(1) The finer particles contain a greater percentage of ignition loss than coarser ones.

(2) The tricalcium silicate will probably be more concentrated in the finer particles than in the coarse ones.

(3) The dicalcium silicate will probably be more concentrated in the coarser particles than in the fine ones.

(4) There seems to be little difference between the fine and coarse particles as to the relative distribution of $4CaO.Al_2O_3.Fe_2O_3$ and tricalcium aluminate.

(5) These facts illustrate the difficulties that are encountered in interpreting and evaluating data showing the relation of particle size to strengths and other physical properties of the cement, especially when no data are presented showing the compositions of the sizes. When the compositions of the sizes being compared are different, it is hazardous to assume that differences in physical properties are the result of difference in particle size.

(6) That apparently the activity of the finer sizes is due not only to their greater surface producing a more rapid and greater reaction with the water than the smaller total surface of an equal weight of coarser particles, but also to the finer sizes being composed largely of the more rapidly reacting tricalcium silicate.

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Notes from the Foreign Press.

Detection and Determination of Free Lime in Cement. By W. MARSCHNER. *Zement*, Vol. 21, p. 489, 1932.

The method of Tananaeff and Kulberg, recently published in "Zeitschrift für Analytische Chemie," is described. This new method has the advantage of giving a qualitative result in 3 to 5 minutes and a quantitative result in 35 to 40 minutes, a great saving of time over the several hours required by the older methods.

The method depends on the formation of yellow mercury oxide from mercuric chloride by calcium oxide, and upon the fact that other calcium compounds do not react with $HgCl_2$ in the presence of $CaCl_2$. The mercury oxide is made to combine with potassium iodide, and the resulting KOH solution is titrated with acid and methyl orange. By using $HgCl_2$ dissolved in absolute alcohol the free lime in cement can be determined. The combined reactions are represented by the equation

$$HgCl_2+CaO+4KI+H_2O=CaCl_2+2KOH+K_2HgI_4.$$

The experimental details are as follows: 0.2 – 0.5 g. of cement is placed in an Erlenmeyer flask with ground-in stopper. Twice the quantity of $HgCl_2$ required to react with the maximum possible amount of free lime is added, with a few glass beads and 20 to 25 c.c. alcohol. It is essential that the alcohol should be free from water. This may be tested by adding a drop of phenolphthalein to the flask and mixing well, when there should be no red tinge. The flask is shaken periodically for 15 to 20

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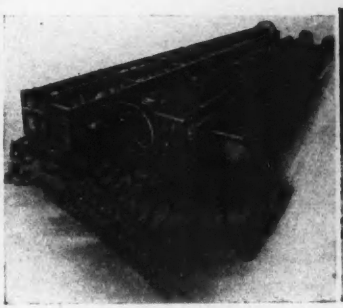

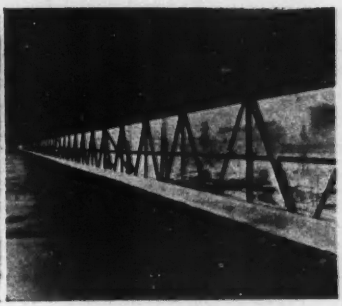

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minutes, during which time the contents become yellow if free lime is present. The contents are filtered, the filter being well washed with alcohol until all $HgCl_2$ is removed. The filtrate is tested for $HgCl_2$ with a few drops of ammonium sulphate solution, with which $HgCl_2$ gives a black precipitate or forms a dark solution. The cement and HgO on the filter are next washed with a saturated solution of KI in dry alcohol, when the HgO dissolves and the filtrate is collected. To this filtrate is added 30 c.c. of water and methyl orange, and the liquid is titrated with N/10 HCl. The percentage of free lime is 0.28 V/W (assuming the acid is exactly N/10), where V is the number of c.c. of acid used and W is the weight of cement taken.

The following qualitative method does not require a microscope. A small amount of dry $HgCl_2$ is placed on a clock glass and covered with cement, and this again is covered with $HgCl_2$. From 8 to 10 drops of dry alcohol are added and the whole is gently warmed. If free CaO is present a yellow colour is formed in 30 seconds. The reaction is very sensitive and will detect 0.02 per cent. of free lime. The following table enables an approximate estimation of the amount of free lime to be made:

Colour	Percentage of free lime
Pale straw yellow	0.02
Straw yellow	0.05
Pale yellow	0.10
Yellow	0.20
Pale brown	0.4
Brown	0.6
Chocolate	0.8
Dark chocolate	1.0
Brownish red	2 to 10

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